



Characterization and Photoreactivity of Titanium Dioxide Nanostructures

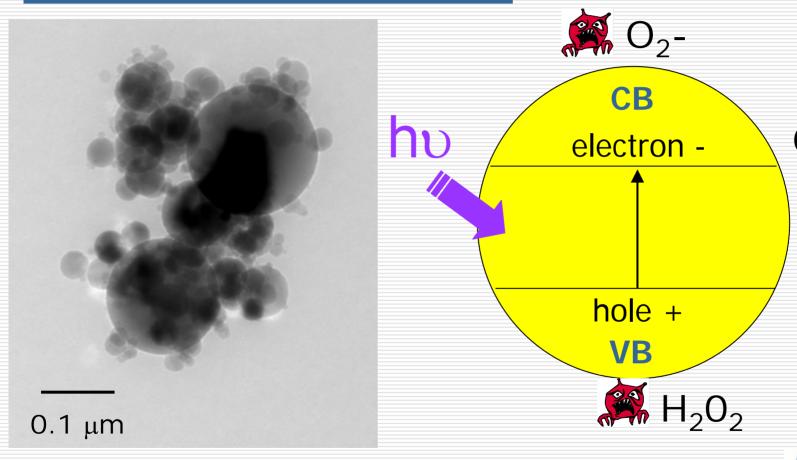
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The Problem

- □ Photocatalytic properties of particulate fillers (TiO₂) affect the service life and durability of polymeric systems.
- Photoreactivity widely varies in TiO₂ materials, depending on their method of preparation.
- Prediction of photoreactivity of these materials is difficult, since the properties controlling photoreactivity are not well understood.
- Each industry/company utilizing TiO₂ has developed their own qualitative methods to evaluate photoreactivity.

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Semi-Conductor Nanostructures





Motivation and Background

TiO₂ Photoreactivity

LOW

HIGH elf-cleaning surfaces

paper
plastics
coatings
sunscreen
(\$9 billion/yr)

self-cleaning surfaces
water purification
chem/bio protection
air cleaning
solar cells



Technical Approach

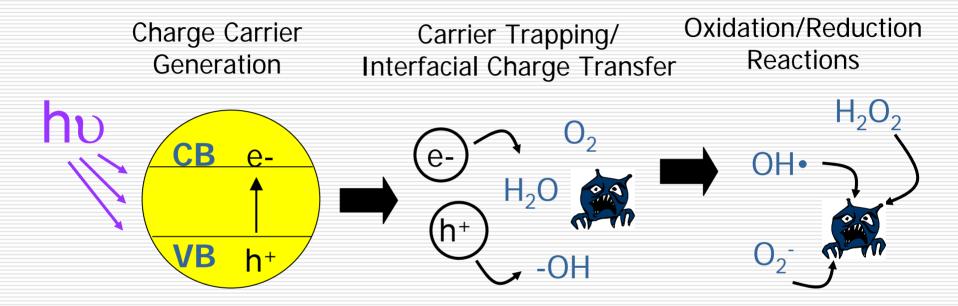
- Develop novel metrologies for the measurement of photoreactivity
- Development of analytical techniques for characterizing bulk and surface properties of TiO₂
- Establish correlation(s) between photoreactivity, material properties and heterogeneous photochemistry, and product-based tests.

Impacts

- Fine tune the manufacture of pigment, i.e. crystal phase, size, and surface treatment, for a specific application.
- Reduce the time-to-market for coatings by using the ability to optimize the choice of pigment for a particular coating.
- Optimize the quantity of pigment used in coatings, possibly resulting in a cost savings.



Measurement Organization



Photoconductivity

Electron Paramagnetic Resonance
(EPR)

THz spectroscopy

Chemical Assays

EPR
THz Spec.
Chemical Assays

EPR Performance Tests

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The Link for Pigmented Systems

- □ Take into account
 - Protection
 - □TiO₂ absorbs UV radiation, preventing direct photochemical attack
 - Degradation
 - □TiO₂ absorbs UV radiation and generates free radicals, which oxidize the binder
 - Physical Effects
 - □Ability to anchor to the binder
 - ■Degree of dispersion



Photoreactivity Program Organization

Characterization

Surface
Size and distribution
Crystal form
Morphology



Photoreactivity Measurements

Photoconductivity EPR*

IPA test*

Chemical assays*

THz spectroscopy

Conductance AFM



Product-Based Testing on Systems

Coatings/polymers
Air cleaners
Antimicrobial surfaces
Photovoltaic cells
Other applications???

Measurement of:

Aggregation Flocculation Dispersion



Material Characterization

- Physical Properties
 - Crystal Phase
 - ☐ Crystalline vs. Amorphous
 - Anatase vs. Rutile
 - Particle Size

Gas Adsorption

Brunauer, Emmett, and Teller (BET) Method

Microscopy

Surface Area

BET

XRD

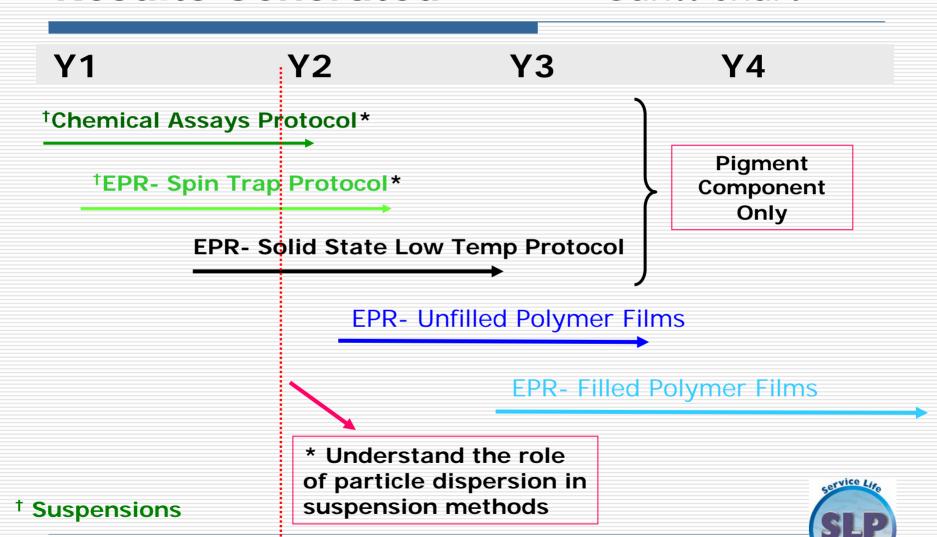
- Chemical Properties
 - Elemental Impurities (e.g. Fe, Cr,Nb)
 XRF
 - Surface Charge
 - ☐ Zeta Potential, Isoelectric Point
 - Surface Functional Groups

Infrared, BET



Results Generated

Gantt chart



Refine and improve current measurements

Chemical Assays

- ☐ Methyl viologen/EDTA Validate Hole/Electron Concentration
 - Photogenerated holes oxidize EDTA
 - Electrons reduce methyl viologen to blue methyl viologen radical
 - Rate of adsorption (λ =602 nm) directly proportional to rate of photochemical reaction
- ☐ Hydrogen Peroxide Measurement Determine Reaction Mechanism
 - During isopropanol oxidation:

$$\square$$
 (CH₃)₂CHOH + •OH

$$\square (CH_3)_2 CHOH + \bullet OH \rightarrow (CH_3)_2 \bullet COH + H_2O$$

$$\Box O_{2^{-}(ads)} + H_{2}O$$

$$\square$$
 (CH₃)₂•COH + O₂ \rightarrow

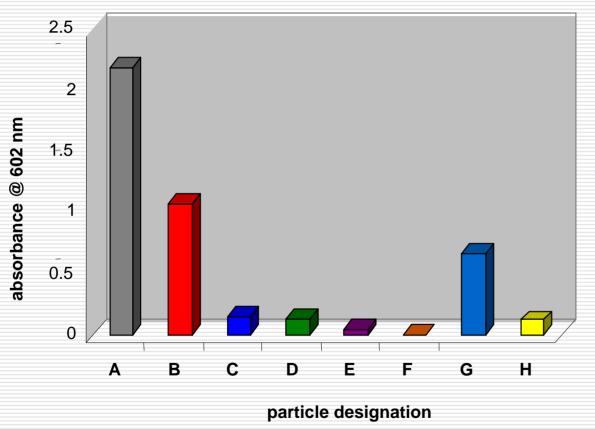
$$(CH_3)_2CO + H_2O_2$$

- o-dianisidine and horseradish peroxidase
 - \square Adsorption at λ =500 nm



Chemical Assays

methyl viologen



1. A - anatase

2. B - rutile

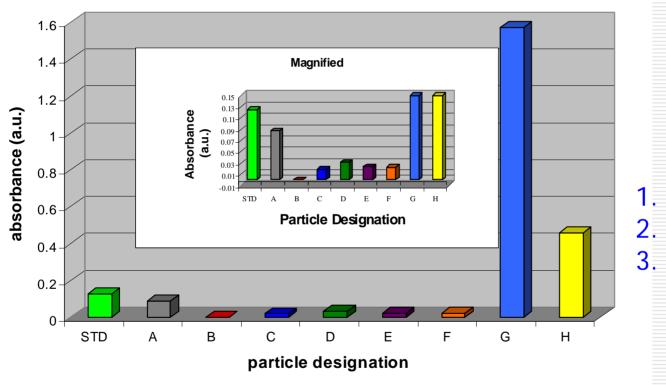
3. C - anatase/rutile

 $I_{\lambda = 602}$ \propto [methyl viologen cation radical]



Chemical Assays

Peroxide-Leuco Crystal Violet/Horseradish Peroxidase



 $I_{\lambda = 590} \propto [leuco crystal violet]$

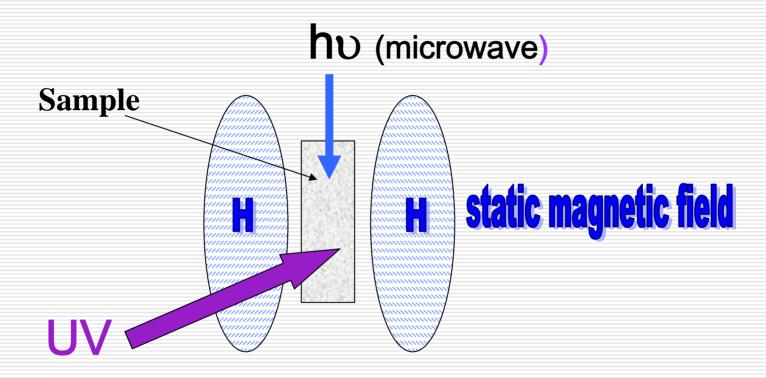
I. G - anatase/rutile

2. _|H - N-anatase

A - anatase



Electron Paramagnetic Resonance (EPR)



 Detection of free radical intermediates, oxidation state/coordination of metal oxide, free radical formation kinetics measurement

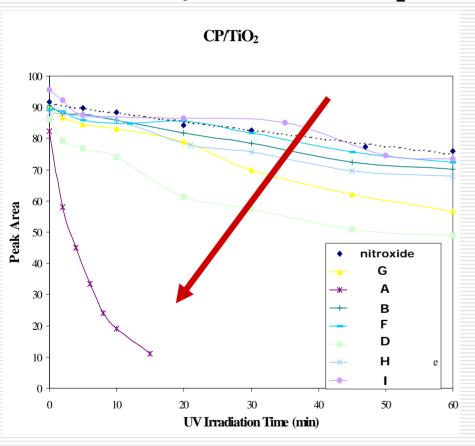
EPR

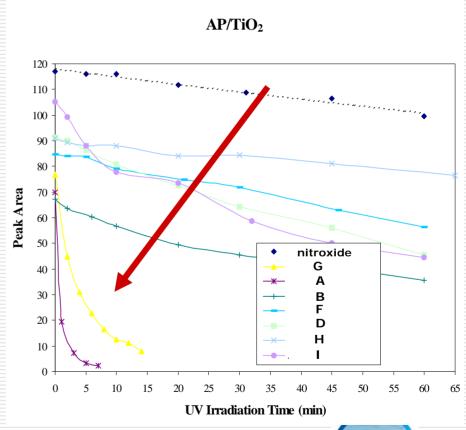
- □ Indirectly measure species with unpaired electrons
 - Use of "spin traps", such as nitroxide, to monitor concentration of specific short-lived free radicals
- Low temperature (77K or lower)
 - Directly identify species with unpaired electrons
 - ☐ Identify species involved in charge transfer processes
 - Determine the corresponding electron-accepting and electron-donating sites
 - Ti+3 and O-
 - Identify oxidation states



EPR: Nitroxide Spin-Trap

Comparison of CP/TiO₂ and AP/TiO₂







EPR: Solid State Studies

- □ EPR was used to monitor changes of the TiO₂ pigments in the solid state at 77K.
- Each pigment revealed a different EPR spectrum.
- Each pigment also had a different response with UV exposure.
- In general, the intensity of select peaks present in the initial pigment specimen increased with increasing UV exposure.

Product-Based Testing

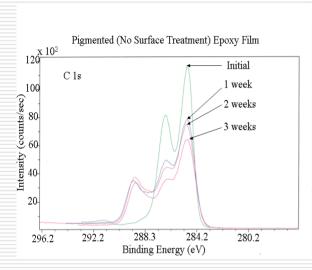
Coatings

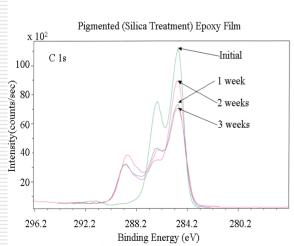
- Monitor pigment changes under UV irradiation
 - create surface oxygen vacancies at bridging sites, conversion of relevant Ti⁺⁴ sites to Ti⁺³ sites
 - Focus on oxygen and titanium
- Monitor polymer degradation under UV irradiation
 - Follow the disappearance and formation of chemical species
- ATR-FTIR
- X-ray Photoelectron Spectroscopy (XPS)
 - Measures x-ray generated electrons from the surface of samples
 - Provides elemental and chemical oxidation state information
- EPR
 - Monitor free radical generation in degradation of polymer in combination with pigment



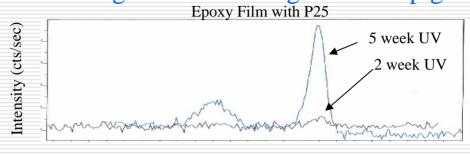
Chemistry

XPS Results-High Resolution

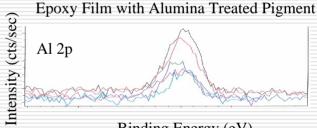




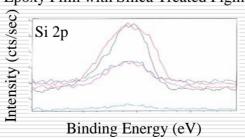
Similar degradation rate regardless of pigment type



Binding Energy (eV)



Epoxy Film with Silica Treated Pigment

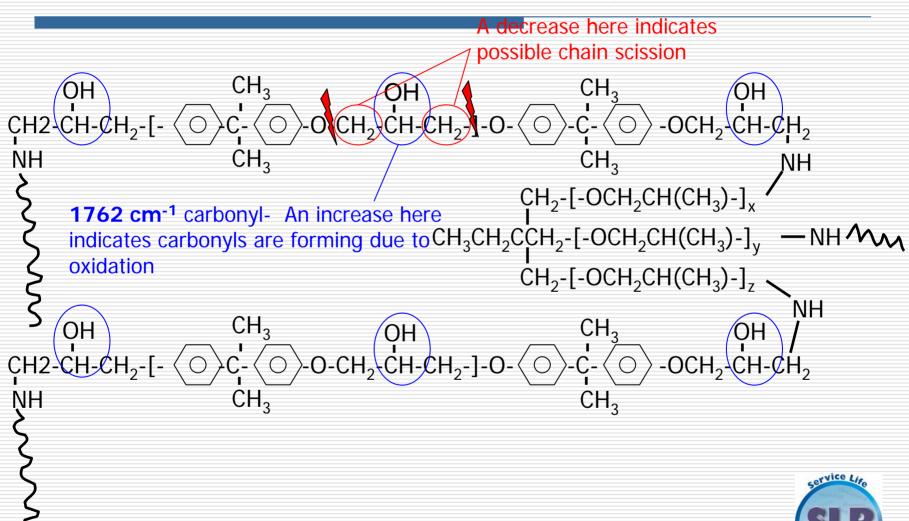


Binding Energy (eV)



Chemical Degradation - IR

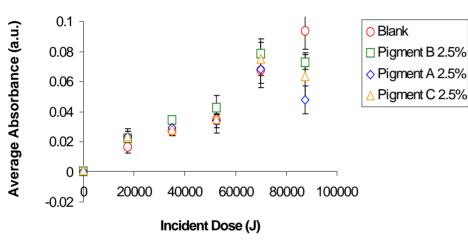
2952 cm⁻¹ aliphatic carbon-



Chemistry

IR Results

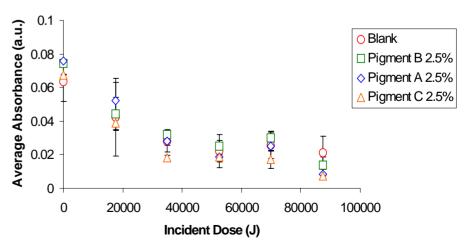
Oxidation Product (C=O at 1762 cm-1)



Degradation rate very similar regardless of pigment type

Other peaks monitored: 1540 and 834 cm⁻¹

Mass Loss (C-H at 2952 cm-1)



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EPR: Polymer Film Studies

- EPR was used to examine filled and unfilled epoxy and acrylic urethane films in-situ with UV exposure.
- New peaks appear in the EPR spectrum with increasing UV exposure.
 - Some peaks are due to the polymer resin
 - Some peaks are due to the pigment
- UV exposed filled acrylic urethane films show greater EPR peak intensity.



Summary

- NIST Focus: Provide tools to understand fundamental aspects of photoreactivity in TiO₂ and insight into conventional performance testing.
- ☐ Chemical assays quantitatively measure the electron/hole concentrations in various systems and can be used to validate other photoreactivity measurements.
- ☐ EPR spectroscopy can identify both the nature and lifetimes of short-lived species in pigments and polymer systems.
- Product-based tests still have an important role in product development.

Acknowledgements

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